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## **Tri-Service Site Characterization and Analysis Penetrometer System Validation of the Membrane Interface Probe**

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# **Tri-Service Site Characterization and Analysis Penetrometer System Validation of the Membrane Interface Probe**

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# Preface

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The work reported herein was funded by the Environmental Security Technology Certification Program. Mr. George Robataille was the technical monitor for the U.S. Army Environmental Center, and Dr. M. John Cullinane, U.S. Army Engineer Research and Development Center (ERDC), was the program manager.

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At the time of publication of this report, Dr. James R. Houston was Director of ERDC, and COL John W. Morris III, EN, was Commander and Executive Director.

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# 1 Introduction

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## Background Information

Chlorinated solvents and fuel related volatile organic compounds (VOC)<sup>1</sup> contaminating subsurface soil and groundwater have caused substantial problems at many sites including U. S. Department of Defense (DoD) installations. Current methods for locating and delineating subsurface VOC contamination during site characterization are time consuming and costly. Traditional site characterization techniques include drilling, sampling, and laboratory analyses. Because placement of soil bores and monitoring wells on a given site is often based on limited geological information, many are placed at less than optimum locations that contribute little to the site investigation. Often, laboratory analysis of the samples obtained from soil bores and monitoring wells are not available for weeks.

To address these problems, the Tri-Services (U.S. Army, U.S. Navy, and U.S. Air Force) cooperated in the development and field demonstration of the Site Characterization and Analysis Penetrometer System (SCAPS) contaminant sensor and hybrid sensor/sampler technologies. The SCAPS consists of a hydraulically operated cone penetrometer system mounted in a custom-engineered truck with onboard computers to provide real-time data acquisition/processing of co-registered geophysical and contaminant sensor data. The truck is capable of pushing instrumented cones to depths greater than 50 meters (m) in nominally compacted soil, providing a variety of information such as subsurface soil stratigraphy, depth to groundwater, recovery of soil and water samples, and in situ measurement of specific contaminants. The SCAPS was also designed to accommodate sensors and samplers for use in collecting data on specific classes of subsurface contaminants. Contaminant sensors/samplers developed to date include sensors for petroleum, oil and lubricants (Aptiz et al. 1992), explosive compounds (Cespedes et al. 1995 and Buttner et al. 1997), heavy metals (Miles, Cortes, and Cespedes 1997), VOCs in vadose zone soils (Myers et al. 1998), VOCs in groundwater (Davis et al. 1997a), and gamma emitting radionuclides (Morgan, Adams, and Ballard 1998).

Under funding from the U.S. Army Environmental Center (AEC), a groundwater sparging device was developed at Oak Ridge National Laboratories

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<sup>1</sup>For convenience, abbreviations and symbols are listed in the notation (Appendix C).



(ORNL) to purge VOCs from groundwater directly into a field portable direct sampling ion trap mass spectrometer (DSITMS). Previous Environmental Security Technology Certification Program (ESTCP) demonstrations of this Hydrosparge VOC sensor with direct push mini-wells have shown that the quality of VOC data produced approximates that of offsite analysis of well water samples collected and analyzed by conventional methods (Davis et al. 1997b; Davis et al. 1998; Davis, Furey, and Porter 1998; and Davis et al. 2001). The Hydrosparge VOC sensor has the advantage of providing onsite, in situ analysis for VOCs without actually removing groundwater from the monitoring well.

A second-generation tool, the Hydrosparge II, integrated the groundwater access of the direct push mini-well and the VOC purging function of the in situ sparge module into a single probe. This integrated system allows multiple subsurface sampling and analysis events during a single penetrometer push while providing geophysical data and through-the-probe grouting. Demonstration of the Hydrosparge II was funded by ESTCP in February 1998. The first field demonstration was executed in July 1998 at the Naval Air Station (NAS) North Island, Coronado, California. The Hydrosparge II probe performed well; however, due to geological conditions, it was unable to collect valid data from 50 percent of the test locations. The ESTCP Management Office approved the suspension of the Hydrosparge II verification demonstration work and initiation of the verification demonstration of the newly developed Membrane Interface Probe (MIP), recently introduced by Geoprobe Systems, Inc. Preliminary laboratory and field tests demonstrated the ITMS-MIP combination was capable of rapid VOC detection and clearly demonstrated that the MIP was capable of multiple VOC sampling events during a single penetration. The U.S. Army Engineer Research and Development Center (ERDC) fabricated a unique hybrid sensor/sampler probe using a modified MIP module provided by Geoprobe Systems, Inc., and an ERDC designed and fabricated geophysical cone sensor with through-the-tip grouting capabilities.

## **Official DoD Requirement Statement**

The DoD has a critical need to demonstrate advanced rapid cost effective technologies to characterize soil and groundwater contaminated by VOCs. The successful completion of this technology verification project will provide the DoD with demonstrated capabilities to characterize a site for subsurface VOC contamination in situ and to delineate zones free of contamination. This project will provide a technical capabilities database for the pursuit of regulatory acceptance and detailed cost analyses for assistance in technology transfer.

## **Objectives of Demonstration**

The purpose of the SCAPS technology demonstration was to generate field data appropriate for verifying the performance of the ITMS-MIP VOC system and to facilitate technology acceptance and use by the regulatory and user communities for field screening of sites for subsurface VOC contamination. To obtain the data required to verify the performance of the SCAPS ITMS-MIP

system for field screening, both primary and secondary demonstration objectives were identified.

The primary objectives of this demonstration were to evaluate the in situ SCAPS technology in the following areas: (a) performance compared to conventional sampling and analytical methods, (b) the logistical and economic resources necessary to operate the technology, (c) data quality, and (d) the range of environmental conditions in which the technology can be operated. The secondary objectives for this demonstration were to evaluate the SCAPS ITMS-MIP system for reliability, ruggedness, and ease of operation. Performance of the ITMS-MIP system was evaluated by comparison to conventional ex situ sample analytical methods (U.S. Environmental Protection Agency (USEPA) Method 8260).

## **Regulatory Acceptance of SCAPS Innovative Technology**

A major obstacle to implementation of innovative site characterization techniques on DoD sites is acceptance of new technologies by both Federal and State regulatory agencies. The Tri-Service SCAPS program has experience with pursuit of regulator acceptance of SCAPS innovative technologies such as the Laser Induced Fluorescence (LIF) petroleum, oil, and lubricant (POL) sensor, the original Hydrosparge VOC sensor (Davis et al. 1998), and the Thermal Desorption sampler (Myers et al. 1999). The final detector for the system, the DSITMS, is the same detector used by the Thermal Desorption Sampler (Myers et al. 1999) and the Hydrosparge VOC sampler (Davis et al. 2001). The DSITMS has been rigorously reviewed by the USEPA Office of Solid and Hazardous Waste (OSHW) (draft SW-846 Method 8265 (USEPA 1994)), the state of California Environmental Protection Agency Department of Toxic Substance Control (certification report in preparation), and the Interstate Technology Regulatory Cooperation (ITRC) Workgroup (ITRC 1997). Another product of this ESTCP demonstration will be the compilation of a high-quality data set that can be used to pursue regulatory acceptance at both Federal and state levels. Primary points of contact for the ITMS-MIP demonstration are given in Appendix A.

## **Previous Testing of the Technology**

The Geoprobe Systems, Inc., MIP was developed for logging VOCs in the subsurface. It is commercially available and has been used for site characterization since 1998. In 1998, the MIP was selected as a tool to be evaluated as a SCAPS probe. The membrane and heater block from the MIP were incorporated into an ERDC SCAPS probe that includes soil classification sensors and through-the-tip grouting. Previous MIP SCAPS field investigations include a demonstration at Alameda Naval Air Station, Alameda, California, completed in August 1998. The contamination at the Alameda site included a complex mixture of petroleum hydrocarbons and chlorinated solvents located within saturated soil

**In-Situ MIP vs EPA 8260 for TCE**

Linear Statistics  
 $R^2 = 0.90$   
Slope = 0.81  
Intercept = 16.2

Legend:  
♦ Alameda  
■ Lake City  
▲ Long Horn

4

## 2 Technology Description

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This section describes the SCAPS ITMS-MIP system including background information and a description of the equipment. General operating procedures, training and maintenance requirements, and some preliminary information regarding the costs associated with the technologies are also discussed.

### Description

The SCAPS truck is the platform for a family of rapid field screening technologies used to determine the spatial distribution of subsurface contaminants. Geoprobe Systems, Inc., developed the MIP as a tool for logging of VOC contamination versus subsurface depth. The integration of the MIP and DSITMS was performed by the ERDC. The ITMS-MIP system is an integrated sensor capable of collecting soil classification data during penetration and performing VOC concentration measurements (regardless of matrix) at multiple, discrete depths during a single penetration. The VOC analytes collected by the MIP are transferred to the surface via umbilical cable tubing for identification and quantification by the DSITMS that is located in the SCAPS truck. The different components of the SCAPS ITMS-MIP system are discussed in detail below.

### Cone penetrometer platform

Cone penetrometry has been widely used in the geotechnical industry for determining soil strength and soil type from measurements of the conical tip force and the cylindrical sleeve friction force on a Cone Penetrometer Test (CPT) instrumented probe. The SCAPS platform uses a truck-mounted hydraulic ram to advance and retract chemical and geotechnical sensing probes. The SCAPS platform provides an 18.2 MT (20-ton) static reaction mass associated with the weight of the truck. The hydraulic push room, containing the rods, hydraulic rams, and associated system controllers, is located in the forward compartment over the truck's center of gravity. Underneath the SCAPS truck push room is a pressure manifold system for rod and probe decontamination. The rear compartment of the truck contains onboard computers for data collection as well as the aboveground components of the SCAPS technology. The combination of reaction mass and hydraulics can advance a 1-m-long by 4.45-cm-diam threaded-end rod into the ground at a rate of 2 centimeters per second (cm/sec) in accordance with ASTM Method D3441 (ASTM 1995), the standard for geophysical

sensing CPT. The rods, various sensing probes, and sampling tools can be advanced to depths in excess of 50 m in nominally compacted soils. As the rods are withdrawn, grout can be transferred from a surface mounted grout pump through a 0.63-cm- (0.25-in.-) diam tube within the SCAPS umbilical cable to hydraulically seal the penetrometer hole.

### **Geophysical cone sensor**

The soil classification sensor used during the demonstrations was integrated with the permeable heated MIP module and a surface mounted ITMS system. However, the geophysical cone sensor is often used as a stand-alone sensor for soil classification. The soil classification sensor consists of a cone tip and a friction sleeve instrumented with a full strain-gauged bridge in a wheatstone configuration. The instrumented elements respond to external axial load during normal probe advancement. The outputs from the instrumented elements constitute the typical electrical cone penetrometer response used for soil stratigraphy identification and classification (Lee et al. 1994). The soil classification data are used to select the depth for sample collection during the MIP penetration.

### **Membrane Interface probe**

The MIP configuration shown in Figure 2 was developed and manufactured by Geoprobe Systems, Inc. (Christy 1997). It can be driven or pushed to the depth of interest and operated to extract and collect a VOC vapor sample. This sample is then transported via a carrier gas within a transfer line to the surface for analysis. The MIP can then be advanced to the next depth of interest and the sample extraction and collection process repeated. Unless the MIP membrane fails, there is no need to retrieve the device between measurements.

The membrane interface portion of the MIP consists of a small polymer port that is permeable to gas but impermeable to liquid. The permeable port is a thin film of tetrafluoro ethylene (TFE) (Teflon, E.I. Du Pont de Nemours & Co.) impregnated onto a stainless steel screen with an area of 37.42 mm<sup>2</sup> and a thickness of 0.76 mm. The permeable port is brazed onto a steel block (Figure 2) that also contains a resistive heater coil and a thermocouple allowing the temperature of the membrane to be controlled and monitored. Increasing the heater temperature increases the rate of adsorption into the membrane, diffusion through the membrane, and evaporation from the membrane surface (Kotiaho et al. 1991) into ultra-pure grade helium carrier gas. This carrier gas is circulated over the back of the membrane through a 61-m transfer line (3.17 mm outer diameter (OD) × 1.57 mm inner diameter (ID), polyether ether ketone (PEEK), Alltech, Inc. part # 35717) to the surface mounted ITMS.

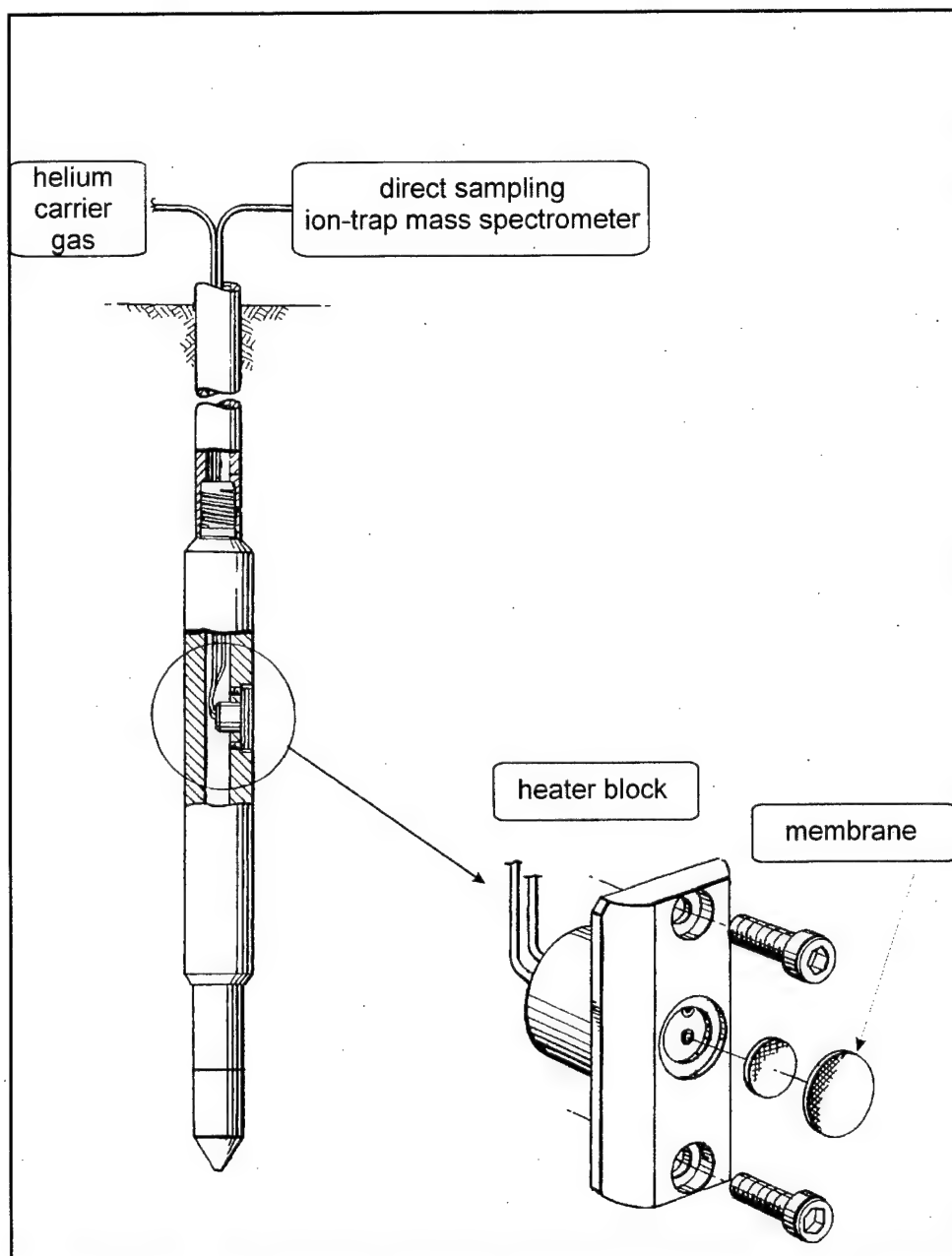


Figure 2. Combined Probe (courtesy of Geoprobe Systems, Salina, KS, from Christy 1997)

### Direct sampling ion trap mass spectrometer

The DSITMS is comprised of a quadrupole ITMS, a capillary restrictor interface, and a variety of sample inlets for use with gas (air and soil gas), soil, and water (Wise and Guerin 1997). The system was one of three models: (a) a Teledyne 3DQ ITMS, (b) a Finnigan ITMS, or (c) a Varian Saturn. Each ITMS is fitted with a 20-cm-long, 100- $\mu$ m internal diameter capillary (J&W part #160-2635) restrictor heated interface (Scientific Information Service, Inc. part

#912000) operated at 105 °C. The capillary interface limits flow into the ITMS to 0.1 to 1.0 mL/min, which is compatible with both electron impact ionization (EI) and chemical impact ionization (CI) sources. Chlorinated solvents were analyzed using EI. Benzene, ethyl benzene, toluene, and xylene (BETX) were analyzed using water CI with the DSITMS operated in the full scan mode (40 to 250 Daltons).

## **Strengths, Advantages, and Weaknesses**

### **Strengths of the membrane interface probe**

The SCAPS ITMS-MIP system was developed to respond to the need for real-time, in situ measurements of subsurface VOC contamination at hazardous waste sites. The ITMS-MIP system performs rapid field screening to determine the presence or absence of subsurface volatile organic contaminants. Interfaced to the MIP, the DSITMS identifies specific VOCs present based on their mass spectra and estimates their concentrations. For soils and groundwater, the DSITMS provides the relative mass of contaminant as a function of depth and lateral distribution. Data obtained from the ITMS-MIP can be used to optimize the placement of conventional soil bores and monitoring wells. In addition, remediation efforts can be directed on an expedited basis as a result of immediate availability of the ITMS-MIP measurement results.

### **Advantages of the technology**

The SCAPS ITMS-MIP system is an in situ field screening technique for characterizing the subsurface distribution of VOC contamination during installation restoration activities. The technology is not intended to be a replacement for traditional soil bores and monitoring wells, but a means to optimize the placement of a reduced number of bores and monitoring wells in order to achieve site characterization and long-term monitoring during remedial actions.

The ITMS-MIP system uses a CPT platform to provide real-time field screening of the distribution of VOC contamination at hazardous waste sites. The current configuration is designed to quickly and cost-effectively distinguish VOC contaminated areas from uncontaminated areas and provide semiquantitative estimates of soil and groundwater VOC contaminant concentrations. This capability allows further investigation and remediation decisions to be made more efficiently and reduces the number of samples that must be submitted to laboratories for costly analysis. In addition, the SCAPS CPT platform minimizes exposure of site personnel and the community to toxic contaminants during site characterization. Use of the CPT platform also minimizes the volume of investigation derived waste (IDW) generated during typical site characterization activities.

The linear dynamic range of ITMS-MIP is partially controlled by the linear dynamic range of the DSITMS. Data presented in Figure 1 show that the ITMS-

MIP can respond to analytes in concentrations ranging over 5 orders of magnitude. These in situ data were collected in real-time without sample dilution. This ability to analyze samples without dilution is possible because of the automatic gain control capability in the newer ITMSs. The ion trap is scanned to determine the number of molecules present. Once the load is determined, a portion of the analyte is allowed into the mass spectrometer. Once mass analysis is complete, the results are corrected based on a portion of the load analyzed. This process is automated and occurs in approximately 1 sec. The ability to acquire data in real-time over a large dynamic range makes the newer ITMS models an ideal detector for the MIP since sample dilution is not an option given the current system design.

### **Limitations of the ITMS-MIP system**

This section discusses the known limitations of the SCAPS ITMS-MIP system, as they are currently understood.

**Truck-mounted cone penetrometer access limits.** The SCAPS CPT support platform is an 18.2 MT (20-ton) all-wheel-drive, diesel-powered truck. The dimensions of the truck require a minimum access width of 3 m (10 ft) and a height clearance of 4.6 m (15 ft). It is conceivable that some sites, or certain areas of sites, might not be accessible to a vehicle the size of the SCAPS truck. The access limits for the SCAPS truck are similar to those for conventional drill rigs and heavy excavation equipment.

**Cone penetrometer advancement limits.** The CPT sensors and other tools may be difficult to advance in subsurface lithologies containing cemented sands and clays, buried debris, gravel units, cobbles, boulders, and shallow bedrock. As with all intrusive site characterization methods, it is extremely important that all underground utilities and structures are located using reliable geophysical equipment operated by trained professionals before subsurface characterization activities are initiated. Nonintrusive cable and pipe location should be conducted even if subsurface utility plans for the site are available for reference.

**ITMS-MIP system limitations.** The DSITMS is operated in accordance with USEPA draft Method 8265. The MIP uses the DSITMS to identify and quantify VOC analytes desorbed from the subsurface. One of the limitations of the DSITMS is that for particular pairs of analytes, the ITMS cannot distinguish between analytes that yield identical mass fragments. For example, the DSITMS cannot distinguish between the different positional isomers of the dichloroethenes (cis- or trans-1,2- and/or 1,1-DCE) because they yield molecular ions of the same mass. Another example is that 1,1,2,2-tetrachloroethane and chloroform (trichloromethane) both yield characteristic ions primarily at masses of 83 and 85 and are therefore reported as an analyte pair. Using the current DSITMS technology, it is not possible to differentiate analytes yielding identifying ions of the same unit mass, therefore such analytes are reported as a sum of the two. It should be noted that the current USEPA laboratory method (USEPA Method 8260) using gas chromatography/mass spectrometry is still not able to differentiate some analyte pairs (i.e. meta- and para-xylene).



**Sampling limitations.** The MIP samples VOCs in direct contact with its heated membrane surface (approximately 37 mm<sup>2</sup>). The sample size or area influenced by the heated membrane has not been studied but is affected by temperature of the membrane, the type of subsurface media (vadose zone soil or saturated soil), and contact time between membrane and soil. Because the sample mass and volume are not known, the ITMS-MIP data are considered to be estimates that are a function of depth and lateral distribution.

**Correlation with validation samples.** The ITMS-MIP data appear to be biased toward detection of VOCs in the saturated zone. Correlations between ITMS-MIP data and validation data yielded an R<sup>2</sup> of 0.95 for saturated soils and R<sup>2</sup> of 0.60 and 0.01 for vadose zone soils. This may be a direct result of the method of calibrating the ITMS-MIP using spiked, saturated sand as discussed in Chapter 4, and since the sampling volume of the MIP is not known.

**Note:** The DSITMS is described as a strong qualitative and quantitative tool for applications described in newly approved EPA Method 8265.

### **Extremely high-level contamination carryover**

The effective dynamic range for the ITMS-MIP system is influenced by the dynamic range of the DSITMS and the potential for carryover or cross contamination of the sampling port and helium transfer line during sampling of a highly concentrated sample (greater than 500 mg/L). The lower limit of detection (LOD) of the ITMS-MIP system during the NAS North Island demonstration was occasionally affected by internal contamination of the transfer line that transports the VOC analytes from the subsurface to the DSITMS. Residues remaining in the sample transfer lines caused carryover of analytes between successive analyses. The effect was less analytical sensitivity and an increase in the system lower LOD. A system blank was analyzed after each in situ measurement event. When carryover was detected, the sample transfer line was purged with helium until the background returned to normal (usually 30 min). Figure 3 illustrates ITMS-MIP recovery to baseline sensitivity for the two probes used in these demonstrations after analyzing calibration standards with concentrations up to 100 mg/L. Note that in all cases for Probe 1 and all but two cases for Probe 2, the blank response immediately after calibration analysis was below the detection threshold for that probe.

The problems encountered with carryover in the Teflon transfer line during the NAS North Island demonstration led to the replacement of the transfer line with a nonsorbing PEEK polymer. Laboratory tests performed before the Savannah River Site (SRS) demonstration confirmed that PEEK tubing transferred analytes from the MIP to the DSITMS up to 100 mg/L without detectable carryover of analytes.

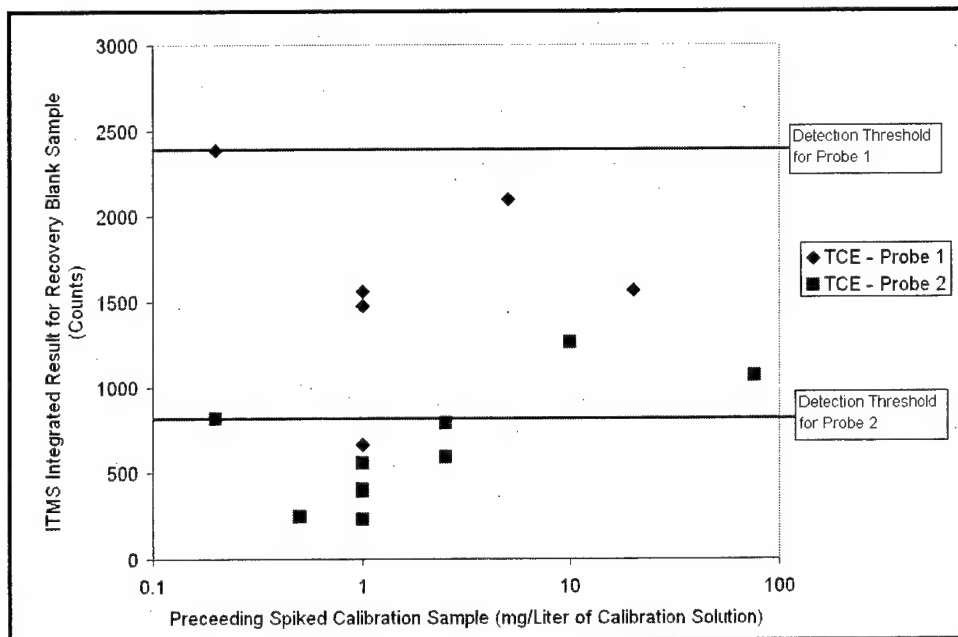


Figure 3. ITMS-MIP blank recovery

Another source of carryover for the ITMS-MIP system is residual VOC from petroleum hydrocarbons in the MIP polymer-coated membrane. However, during field trials at Alameda Naval Air Station and SRS, a few minutes of purged heating of the polymer membrane quickly restored the MIP to its baseline sensitivity and reproducibility.

### MIP membrane failure

Continuous pushing in sand and gravel soils can cause the Teflon polymer membrane coating to become scratched and fail. A drop in pressure in the transfer line running from the MIP to the ITMS indicates the loss of integrity of the membrane. For the MIP used in this demonstration, membrane failure occurred only once in six field trips after hundreds of pushes. The membrane could not be patched successfully in the field. The stainless steel screen was removed and sent back to Geoprobe Systems for repair. This resulted in a loss of 2 days work while a backup MIP was sent as a replacement from the ERDC. A new port with a field replaceable membrane is now available from the manufacturer.

## Factors Influencing Cost and Performance

The costs incurred during operation of the ITMS-MIP system include labor and equipment costs. The equipment costs, discounting the capital cost of the SCAPS truck, are the cost of the DSITMS and analytical supplies and maintenance of the SCAPS truck. The major cost associated with the ITMS-MIP system operation is labor. Normal operation of the sensor requires three to four individuals: the CPT operator and helper, the electronics instrumentation operator,

and the ITMS analyst. Costs are normally broken down to a cost per ITMS-MIP sensing event (considered a production unit). The majority of the time required to perform a single sensing event is the time required to push the MIP to the required depth and desorb the sample. The time required to push and retract a probe to depth is the primary factor determining the per unit cost associated with an ITMS-MIP sensing event.

## 3 Site Descriptions

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### Site Selection Criteria

Two sites were investigated during the field phase of this demonstration. Sites were selected in different geographic locations to facilitate wide exposure to user and regulatory communities. Sites were selected based on the following criteria:

- a. Known VOC contamination in concentrations detectable by ITMS-MIP system.
- b. Site topography suitable for SCAPS truck access and maneuvering.
- c. Soil types, cataloged in previous soil bores, suitable for investigation using CPT technology, and sufficiently complex subsurface geology to demonstrate the advantage of rapid onsite analysis compared to conventional site characterization practices.

The two sites selected were:

- a. Naval Air Station North Island, Coronado, California, July 1999 and April / May 2000 (cost demonstration).
- b. DOE Savannah River Site, Aiken, South Carolina, September 1999.

### Naval Air Station North Island Site history

NAS North Island is part of the largest aerospace-industrial complex in the Navy. It includes Naval Amphibious Base Coronado, Outlying Field Imperial Beach, and Naval Air Landing Facility, San Clemente Island. The complex's 2,024 ha (5,000 acres) in San Diego bracket the city of Coronado. The NAS North Island is host to 23 squadrons and 75 additional tenant commands and activities, one of which, the Naval Aviation Depot, is the largest aerospace employer in San Diego, California. The NAS North Island was commissioned a Naval Air Station in 1917. The air station resembles a small city in its operations. The NAS North Island provides police and fire departments, operates large factories such as the Naval Aviation Depot that employs 3,800 civilians, and provides parks, beaches, housing, and recreation areas for military personnel.

The site selected for the ITMS-MIP system verification demonstration was near Buildings 379 and 397 at the Naval Aviation Depot (Figure 4). The site is located in the northeast quadrant of NAS North Island and is surrounded by three buildings: Building 379 to the east, Building 397 to the west, and Building 391 to the south. Jet engine tests and maintenance are conducted in Building 379. Numerous former and existing underground storage tanks (UST) are located within, between, and around Buildings 379 and 397. Buildings 379 and 397 overlie a previously delineated light non-aqueous phase liquid (LNAPL) plume. Building 391 is down gradient from this plume (OHM Remediation Services Corp. 1997).

Jacobs Engineering Group, Inc. (1991), conducted initial site assessment of potential UST leaks in 1991. Seven borings and three monitoring wells indicated contamination in the area around and below the buildings. Contamination was identified by total petroleum hydrocarbons (TPH) in soil and benzene in groundwater. Free product LNAPL was detected in one of the initial three monitoring wells. Based on the initial results, Geosciences (1993) conducted further site assessment during 1993. Ten soil borings and nine monitoring wells were installed and sampled. Total petroleum hydrocarbon contamination was detected in many of the soil samples and LNAPL was detected in two of the monitoring wells (OHM Remediation Services Corp. 1997).

Based on these results, an LNAPL removal system was designed. During initial construction of the LNAPL removal system in 1996, the extent of the LNAPL contamination was found to be four times greater than originally estimated. Construction was halted and the extent of LNAPL contamination was further investigated and delineated in the summer of 1997. After the discovery of TCE in a number of monitoring wells, OHM Remediation Services Corp. recommended additional site characterization and a reevaluation of the proposed site remediation plan.

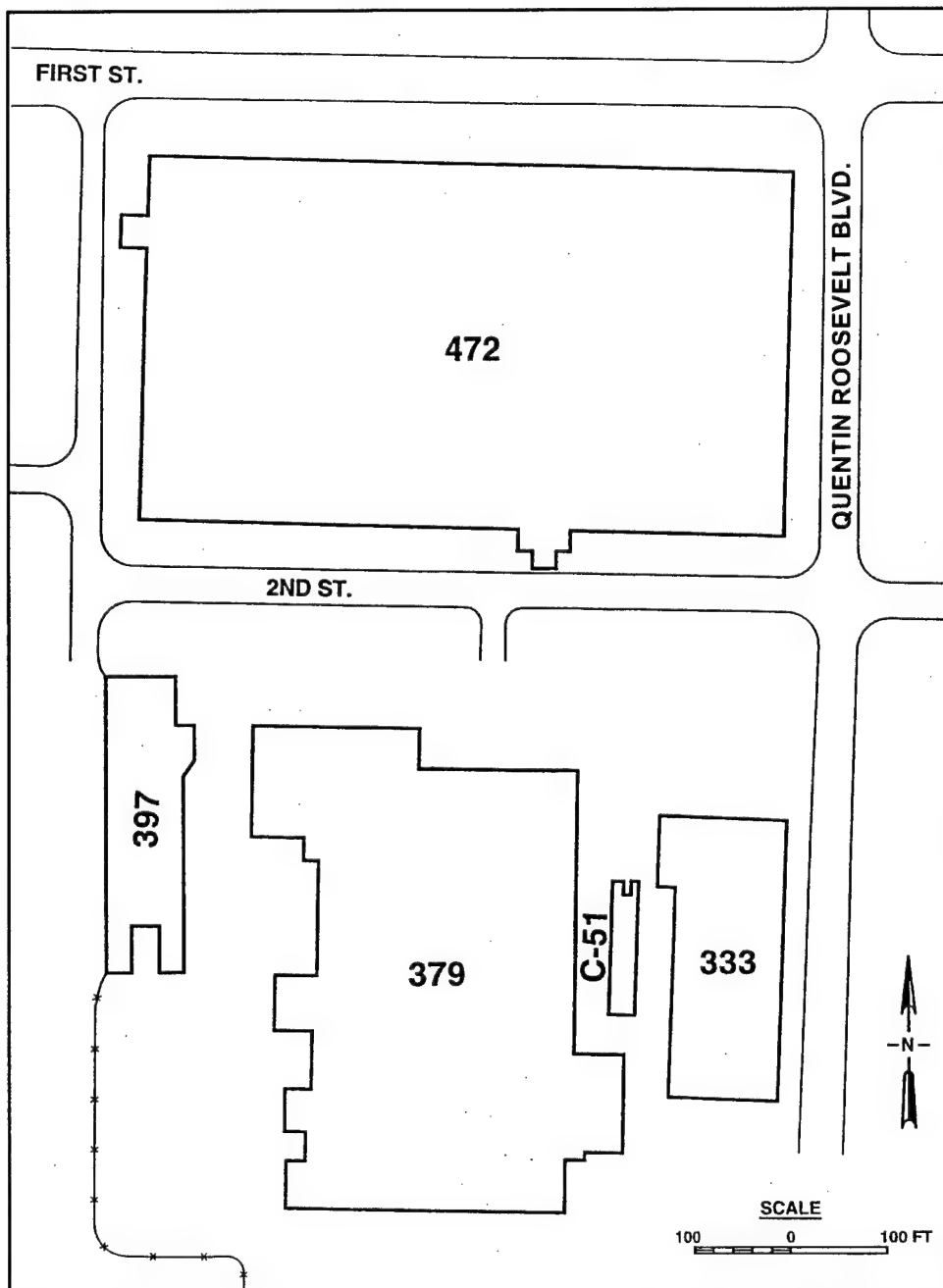


Figure 4. Naval Air Station North Island demonstration site

### DOE Savannah River Site history

The SRS is a 917-km<sup>2</sup> (354-sq-mile) Department of Energy facility located near Aiken, South Carolina. The site selected for the ITMS-MIP demonstration was in the A/M area (Figure 5). The A/M area is a reactor fuel and target assembly area. From the 1950s through the 1980s, approximately 3.5 million pounds of waste solvent, primarily TCE and PCE, were discharged to the A-14 outfall and the M area settling basin. Releases of large amounts of TCE and PCE

led to significant vadose and saturated zone contamination in both dissolved and free phase form (i.e. dense non-aqueous phase liquid, DNAPL). In late 1997 and in 1998, additional soil bores were taken in the A/M area to better characterize the extent of the DNAPL contamination. Soil borings were accomplished by rotosonic drilling, and cores were collected continuously from surface total depth. Depending on the location, total depth was either the top of the Green Clay aquitard (30.5 m BGS) or the top of the Crouch Branch Confining Unit (48.8 m BGS).

Previous investigations of the vadose zone had indicated that the residual DNAPL was confined to fine-grained layers of silt and clays. The results of the 1997/1998 work indicated that no large pools of DNAPL existed in the investigation area. However, TCE and PCE were detected at measurable levels in the clay and sandy clay formations as deep as 48.8 m BGS. The highest levels of contaminant were detected in thin layers of clay less than 0.3 m thick.

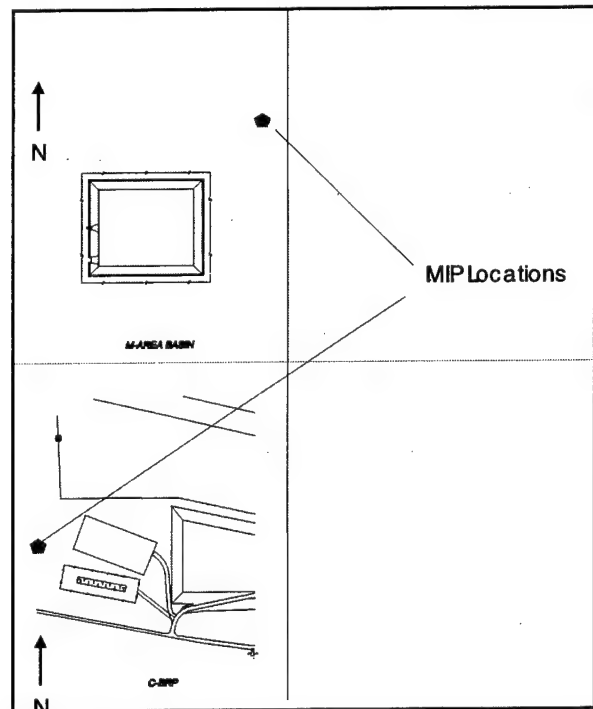


Figure 5. DOE Savannah River Site demonstration site

## Site Characteristics

### Naval Air Station North Island, Coronado, California

Previous investigations have identified two primary geologic units at NAS North Island: an upper well-graded sand to silty sand underlain by a poorly graded sand to silty sand. The upper unit of well-graded fine to medium sand and silty sand contains some coarse grains and is up to 20 percent silt. The upper unit extends from the surface to approximately 4.6 to 6 m (15 to 20 ft) BGS. The upper unit is constructed land that was hydraulically placed for the development of NAS North Island. The lower unit is native land formed by deposition in a near shore environment (Geosciences 1993).

Groundwater at the site appears to flow toward the north-northwest. The average hydraulic gradient across the site has been reported to be 0.0017 m/m (0.0017 ft/ft), and slug tests have measured the hydraulic conductivity to be 0.04 m/day (0.12 ft/day) in the lower geologic unit. These data have been used to conclude that the surficial aquifer is unconfined (Geosciences 1993).

## **DOE Savannah River Site, Aiken, South Carolina**

The SRS lies within the southeastern coastal plain. Interbedded sands, silts, and clays that are typical of a shallow marine depositional environment characterize the coastal plain. Within the SRS, the sediments of the coastal plain have been grouped into three aquifers: the Floridan, the Dublin, and the Midville Aquifer Systems. Within the vicinity of the A/M area, the three aquifer systems coalesce and are delineated as two distinct units called the Floridan/Midville system. The hydrostratigraphy in the A/M area consists of, in descending order, the Steed Pond Aquifer, the Crouch Branch Aquifer, and the McQueen Branch Aquifer (Jerome et al. 1998). The Green Clay confining zone in the M area separates the Steed Pond from the Crouch Branch. The ITMS-MIP demonstration was conducted in the vadose zone above the Steed Pond and Crouch Branch Aquifers.

Previous investigations at the site indicate that sufficient DNAPL was released to penetrate the vadose zone and capillary fringe. The current conceptual model (Jacobson et al. 1996) includes the downward flow of DNAPL being arrested by a capillary barrier referred to as the Green Clay confining zone. Based on the 1997/1998 investigations, the DNAPL is believed to migrate along this barrier.

## **Site-Specific Influences**

The SCAPS ITMS-MIP system was evaluated under varying site conditions to determine if specific site conditions could be identified that affected system performance. Surface anomalies such as steep sloping terrain, paved surfaces, and permanent structures prevented the deployment of the SCAPS ITMS-MIP at some locations and were considered a logistics problem, not a technological problem.

Site conditions that varied during the deployment of the ITMS-MIP system were identified as variables and thus as potential problems. The specific variables identified at the demonstration sites were the number of subsurface interrogations per push location, soil type, saturated versus unsaturated soil, and seasonal temperature differences.

The number of subsurface interrogations per push location was not found to affect the performance of the ITMS-MIP system if adequate care was taken to remove (flush with carrier gas) analyte vapors from system transfer lines between sample interrogations. Since analyte vapors must be removed from system transfer lines to prevent cross-sample contamination, continuous push sampling was not evaluated and is not recommended.

The type of soil undergoing evaluation for VOC contamination was found to affect the correlation with validation samples. At NAS North Island, a "silt mix" soil exhibited an  $R^2$  correlation of 0.05, while a "sand" soil exhibited an  $R^2$  correlation of 0.74. The effect of soil type on ITMS-MIP performance was also observed at the SRS. The effect of soil porosity was not investigated during this



study, but it is thought to contribute to the variability of ITMS-MIP system performance.

The water content of the soil was also found to affect the ITMS-MIP system performance. The in situ ITMS-MIP deployed in the saturated zone of NAS North Island exhibited an  $R^2$  correlation of 0.95 with water validation samples, as opposed to an  $R^2$  correlation of 0.60 for vadose (unsaturated) zone deployment. The ITMS-MIP system was shown to provide optimal performance in saturated soil deployments.

The effects of site temperature did not produce a noticeable effect on ITMS-MIP performance. However, cold temperatures may cause vapor analytes to condense in long cold transfer lines. The effects of varying cold temperatures on analyte transfer were not evaluated during this study.

## 4 Demonstration Approach

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This chapter discusses the demonstration objectives, factors that must be considered to meet the performance objectives, sampling design, and data analysis used to evaluate the results of the demonstration.

### Performance Objectives

The primary objectives of this demonstration were to evaluate the ITMS-MIP system in the following areas: (a) performance compared to conventional sampling and analytical methods, (b) logistical and economic resources necessary to operate the technology, (c) data quality, and (d) range of applications in which the technology can be operated.

### SCAPS ITMS-MIP technology comparison to conventional methods

The ITMS-MIP system performance was validated by collecting soil and water samples from within 0.15 m (6 in.) of the ITMS-MIP in situ measurement and sending the samples to an offsite laboratory for analysis by USEPA Method 8260. The in situ ITMS-MIP system data and EPA Method 8260 data were evaluated and compared using least squares linear regression over the entire concentration range of data collected by each method at every site investigated.

The ITMS-MIP system produced data that are reduced to concentration units of milligrams per liter of calibration solution as described in the section on ITMS-MIP analytical procedures. Comparisons to validation well water samples were done with a straightforward linear regression between the ITMS-MIP in situ data (mg/L) and the co-located well water data (mg/L). For soil samples, the comparative regressions were between the ITMS-MIP data in milligrams per liter of calibration solution and the soil validation sample data in milligrams per kilogram of soil on a wet weight basis.

Another approach for evaluating the soil data might be to convert the ITMS-MIP data from a water based value to a wet weight value. Since the validation samples were retrieved from the subsurface, they could be weighed easily. However, the mass and volume of the MIP sample are not known. One method of converting the ITMS-MIP analysis results from a water basis to a wet weight basis would be to assume that the volume of water present in the soil could be estimated

by the soil's porosity. Making this assumption yields the following conversion equation:

$$C_w \theta / \rho_s = C_s \quad (1)$$

where

- $C_w$  = concentration water basis (mg/L)
- $\theta$  = soil porosity
- $\rho_s$  = soil bulk density
- $C_s$  = concentration wet weight basis (mg/kg)

The absolute soil porosity and density are also unknown for the scale of MIP measurement. Instead of trying to assign values based on some arbitrary method (i.e., using CPT soil type), let  $C_s$  be the validation sample analysis result and  $C_w$  be the MIP sample analysis result. Then:

$$C_w(\text{MIP}) \theta / \rho_s V_{\text{val}} / V_{\text{MIP}} = C_s(\text{Validation Sample}) \quad (2)$$

where

- $V_{\text{val}}$  = volume of validation sample
- $V_{\text{MIP}}$  = volume of the MIP sample

Comparing validation results on a wet weight basis to ITMS-MIP results on a water weight basis would yield a slope that includes the ratio of soil porosity to density and of validation sample volume to MIP sample volume. This approach was not applied to the data in this report. The raw data from each site are found in Appendix B.

## Economic considerations

The general logistics and economics associated with SCAPS CPT operation are known from previous work performed by the ERDC SCAPS system and from work performed from 1995-2000 by the three USACE District SCAPS CPT trucks performing LIF and other site characterization investigations. Cost comparisons between the SCAPS deployed ITMS-MIP technology and conventional methods of subsurface VOC detection (i.e., soil boring/monitoring well installation, sampling, and analysis) were made based on actual ITMS-MIP production rates from the May 2000 NAS North Island deployment. Costs associated with conventional site characterization were estimated based on an investigation scenario projected by the NADS North Island Remedial Project Manager.

## Data quality

Data quality was ensured by strict adherence to the demonstration's Quality Assurance Plan (U.S. Army Engineer Research and Development Center (ERDC) 1999a,b) for field analysis. Verification samples were taken for offsite laboratory

analysis at a rate of 18 to 20 percent. Data quality issues will be discussed in detail in the chapter on ITMS-MIP system performance assessment.

### **Range of usefulness**

The range of usefulness of the ITMS-MIP system was demonstrated at the two sites utilized in this demonstration. In addition, the technology was transferred to the Navy Public Works Center San Diego SCAPS program and to the three USACE District SCAPS programs during fiscal years 1999 and 2000. As discussed previously, there are limits to the ability of a penetrometer truck to push to groundwater at some locations, and DSITMS technology cannot differentiate some VOC analytes and isomer pairs.

## **Technical Performance Criteria**

### **Target compounds for ITMS-MIP analysis**

The ITMS-MIP system can be used as a field screening tool to rapidly determine the location and relative extent of subsurface VOC contamination in the vadose and saturated zones. Desorbed VOC gases are collected in situ, minimizing the number of physical samples and offsite laboratory analyses. The DSITMS, used as a detector, can detect the 34 VOC analytes included on the EPA Target Compound List found in Table 1 of Draft Method 8265 (Wise et al. 1997). While method sensitivity varies by analyte and with periodic changes in DSITMS performance, lower limits of detection in groundwater are generally 100 to 300 µg/L.

### **Reliability and ruggedness**

The ITMS-MIP system consists of two components, the MIP probe and a DSITMS. The complete system has been field demonstrated at five different VOC contaminated sites, including the two sites investigated during this ESTCP sponsored demonstration. The technology is relatively young, but components of the system have been available and used in the field for some time. For example, DSITMS has been used since prior to 1995 in the ERDC SCAPS truck and since 1998 in the USACE District SCAPS trucks. During this time the DSITMS has been quite reliable. The geophysical cone sensor has been used by the SCAPS program from before 1991 and, in general, is used worldwide by the geotechnical community. The MIP has been in the field since 1998. During this demonstration there were issues regarding durability of the membrane with use over time and with the effort and downtime associated with replacing the membrane. The manufacturer has redesigned the membrane block to house a membrane that is easily replaceable in the field.

## **Ease of use**

Typically, a four-person crew is employed to complete all aspects of ITMS-MIP system field operations: a field site manager, two push-room personnel, and a DSITMS operator. SCAPS operation includes a large part of the field activities associated with standard geotechnical CPT technologies. The push-room personnel, a primary SCAPS operator, and a helper carry out these activities. The ITMS-MIP system operator requires a background in science and ITMS theory in addition to detailed training with each of the system components to be able to maintain the system and to make field repairs. In addition, the ITMS-MIP system operator should have experience in VOC analysis and in the preparation of standards and calibration curves.

## **Versatility**

During a single penetration, the ITMS-MIP system will collect VOC data at multiple depths combined with continuous soil stratigraphy information. The system uses the DSITMS as the VOC detector to qualitatively identify VOC contaminants and estimate their concentration. These field screening data can be used to make decisions regarding remediation and monitoring well/soil bore placement and design.

## **Off-the-shelf procurement**

Standard CPT technology is commercially available. The standard geophysical cone sensor for stratigraphy is commercially available from a number of sources. The MIP is available from Geoprobe Systems, Inc. Field portable ITMS has been commercially available for onsite analysis for several years. Information currently available in the open literature makes it possible for anyone interested in using DSITMS to modify commercially available ion trap mass spectrometers to perform DSITMS (Wise and Guerin 1997, Wise et al. 1997). Assembly of system components and umbilical cable fabrication requires personnel skilled in the art of penetrometer probe system integration.

## **Maintenance**

The SCAPS Operations Manual (Koester et al. 1994) details operations and maintenance items for the SCAPS CPT equipment. Briefly, maintenance falls into three categories: basic truck systems, CPT systems (hydraulic, grout pumping, and ram systems), and VOC-sampling systems. The Operations Manual also covers the CPT, associated computers/electronics, soil and water samplers, and the LIF probe. The operation and maintenance of the ITMS-MIP deployed during this demonstration is not addressed by Koester et al. (1994).

The DSITMS requires routine cleaning and maintenance of the instrument. Based on laboratory and field experience, with constant use, ion trap instrument cleaning would be required about every 3 to 4 months and require 2 to 4 hr downtime. The ITMS filaments that produce ions and the electron multiplier that

detects ions and produces the actual DSITMS response require replacement at about the same interval. The manufacturer or a trained ITMS operator should perform maintenance.

The MIP sensor (Figure 2) requires little maintenance. A visual inspection of the membrane prior to deployment and measurement of carrier-gas flow rate during operation are required to ensure the integrity of the transfer lines and the MIP membrane. A drop in carrier-gas flow rate usually indicates a membrane failure. If the membrane is found to be defective, a new membrane can be installed easily in the field using a special wrench supplied by the manufacturer. A visual inspection and a continuity check of the thermocouple and heater wires are also required to ensure the integrity of the heating and temperature monitoring elements.

### **Process waste**

The ITMS-MIP system does not bring soil to the surface in the form of auger cuttings, as do conventional drilling methods. However, investigation-derived wastes will be generated during the process of pressure cleaning the rods and probe during retraction and during calibration of the ITMS-MIP system. Pressure cleaning rinse water and calibration waste are placed in 208-L (55-gal) drums. The drums are labeled and stored onsite for appropriate disposal by facility personnel. Often this rinse water can be analyzed onsite using the DSITMS. If this effluent has nondetectable levels of VOC analytes, the effluent may be discharged on the site. To date, analysis of said rinse water for VOC contamination has consistently been at nondetectable levels. Data collected indicate that the wastewater production rate for rod decontamination is approximately 19 L per 15.2-m (5 gal per 50-ft) penetration.

## **Sampling Procedures**

Standard sampling procedures for the ITMS-MIP system demonstration were implemented to ensure the consistency and integrity of both the ITMS-MIP system data and the results of the verification sample analyses. The sections that follow detail the sample collection procedures necessary to meet demonstration objectives. Careful adherence to these procedures was necessary to ensure that sample data collected using ITMS-MIP system were comparable to Method 8260 (U.S. Environmental Protection Agency (USEPA) 1995) as a screening technique for determining subsurface distribution of VOC contamination. Sampling procedures are discussed in greater detail in the Technology Demonstration Plans (ERDC 1999a,b).

### **Selection of sampling locations at the demonstration site**

Sampling locations for the ITMS-MIP were selected at each site based on knowledge of previous remedial investigation results. Information unique to each

demonstration site is found in the Technology Demonstration Plans (ERDC 1999a,b).

### **Soil classification procedures**

The soil classification scheme used by the SCAPS CPT system was devised to identify the types of soils penetrated with the use of combinations of stress results from the sleeve friction force and cone tip force strain gauge sensors (Olsen 1988). Computer algorithms convert this information into a soil class number (SCN) that corresponds to general soil types. For example, a SCN from 0.5 to 1 corresponds to typical clay while the SCNs ranging from 2 to 4 indicate sand. These parameters are mapped onto soil classification charts to produce a continuous vertical profile graphic representation of the stratigraphy push. During operation, soil class information was collected continuously during the MIP push. The geophysical data may be used in real-time to select sampling depths.

### **MIP sampling procedures**

As with other CPT platform sampler/sensors, the MIP was advanced into the soil at the end of successive lengths of 1-m push pipe collecting soil classification data as the push progressed. Once the MIP reached sampling depth, probe advance was halted and the MIP was heated to volatilize any VOC contaminants from the soil in contact with the membrane. Simultaneously to initiating the membrane heater, the DSITMS was triggered to begin analyzing the carrier gas every second for a period of 3 to 4 min. The MIP was then turned off or kept on based on the DSITMS analysis result. Keeping the membrane hot in conjunction with continuous flushing of the transfer line between data acquisition events prevented the system from being saturated by VOC analytes and biasing future measurements with carryover contamination. Blank and calibration check standard were run as a standard operational procedure before and after each run in order to keep track of carryover and system response and stability. Controlled, intermittent membrane heating is desired when contaminant concentrations were expected to be near the lower limit of detection. The MIP was then pushed to a new depth and the sampling process repeated. The MIP was not retracted between sampling events unless the membrane failed.

### **Verification sampling procedures**

Verification samples were obtained from soil cores collected adjacent to selected MIP penetration locations and were processed according to the method developed by Hewitt (1994) and now included in USEPA SW-846 Method 5035. Approximately 4 mL of soil were immediately subsampled from the core into a preweighed 20-mL VOC vial containing 5 mL of methanol. The vial was sealed using a Teflon-lined cap, and the sample and vial were weighed to determine the soil sample weight. The sampling procedure ensured the integrity of any VOC contaminant analytes and was essentially the first step of Method 8260 (USEPA 1995). Verification samples were stored and shipped at 4 °C.

## Analytical Procedures

The analytical procedures used during the demonstration include both the ITMS-MIP in situ measurement method and the USEPA Method 8260 used to analyze verification samples.

### ITMS-MIP analytical procedures

This section provides a brief overview of the ITMS-MIP analytical method. Details of the direct sampling ion trap mass spectrometer operation are reported in Wise and Guerin (1997) and Wise et al. (1997).

**DSITMS operation.** Chlorinated solvents were analyzed using EI, and BTEX were analyzed using water CI. Since there is no separation technique prior to sample introduction into the DSITMS, the resulting mass spectral data consist of a series of scans containing ions that indicate the presence of VOC analytes (Wise and Guerin 1997). Individual compounds are identified and quantified based on ions of selected masses (Figure 6) indicative of the individual compound (i.e.,  $m/z$  130/132 for TCE by EI and  $m/z$  79 for benzene by water CI). During data collection, the DSITMS was operated in the full scan mode (40 to 250 Daltons), acquiring data from the MIP every second for 3 min. Data acquired during calibration were reduced by integrating a fixed number of mass spectral scans (typically 80 to 100 scans) of the specific ions for a given analyte (USEPA 1994). Data acquired during the ITMS-MIP analysis were reduced in an analogous manner to the calibration standards and were quantified based on the calibration curves discussed in the following sections.

**Calibration.** During operation, the DSITMS was first calibrated in a stand-alone mode. Typical linear calibration curves for VOC analytes of interest extended over three to four orders of magnitude. Once the ITMS operation was verified, it was coupled to the MIP via the PEEK transfer lines. The carrier-gas flow rate was set to a nominal value from 80 to 120 mL/min. The carrier-gas flow rate was monitored and adjusted to remain constant throughout MIP operation. Once the flow rate was set, the coupled ITMS-MIP system was calibrated utilizing a jig containing spiked #2 blast sand (Figure 7). Once the calibration jig was filled, the membrane heater and DSITMS were simultaneously initiated. This method, though a crude approximation of the wide variety of subsurface soil conditions, does allow calibration of the ITMS-MIP system. It should be noted that mixing the sand and spiked water, particularly at low analyte concentrations, could lead to wide variation in the calibration data. Hence, caution must be taken when developing the calibration curve.



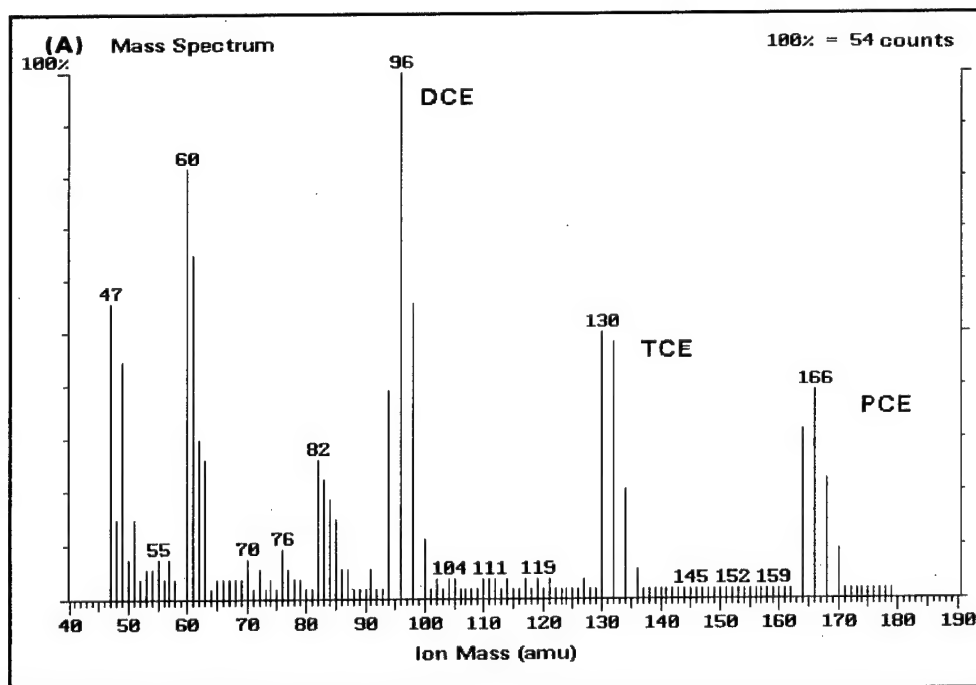


Figure 6. Example DSITMS ion scan

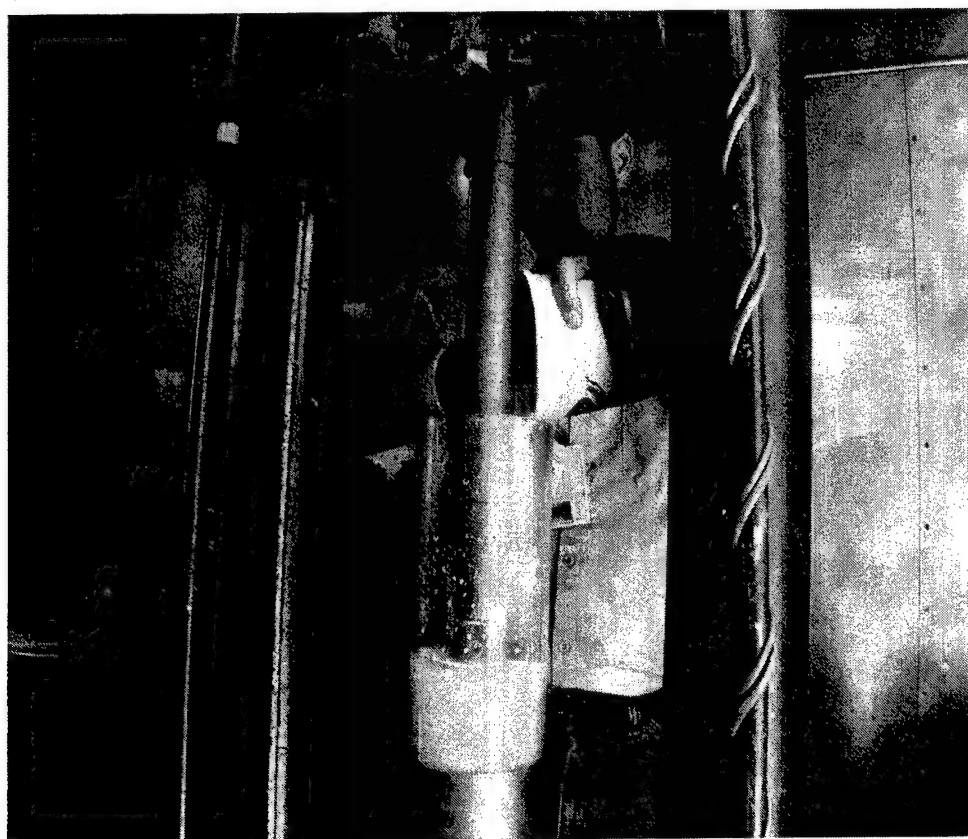


Figure 7. ITMS-MIP calibration

The spiked water is made by injecting an amount of stock standard solution into 250 mL deionized water. The standard solution is made of the analytes of interest, which are prepared by injecting neat (99 percent) VOC analytes into a 10-mL volumetric flask containing approximately 7 to 8 mL methanol. Care is taken to ensure that the neat analyte is dropped directly into the methanol and does not touch the unwetted glass surface of the volumetric flask. The stock solution is prepared in the concentration ranges of 1 to 5 mg/mL. Multiple analyte mixtures in a single stock solution are used as long as no analytes yielding identical mass to charge ratios are mixed. Details of VOC stock solution preparation can be found in EPA Method 8260.

A system blank check and single calibration check standard were performed before and after each set of in situ measurements. Daily calibration check standards and performance evaluation check standards were analyzed to ensure data quality.

Field demonstrations have shown that some sites are very heterogeneous in subsurface soil composition. The soil matrix effects appear to be much larger in the vadose zone than in the saturated zone. Hence, it may be necessary at heterogeneous sites to calibrate the DSITMS for multiple soil materials that are representative of various subsurface strata materials.

**System detection limit.** The ITMS-MIP system detection limit is related to the DSITMS detection limit. Instrument noise, background, and sensitivity were determined using calibration samples prepared using standard analytical techniques immediately prior to each field demonstration.

Lower LOD were calculated using USEPA methods (USEPA 1984). For these determinations,  $n$  replicate measurements of a low but detectable analyte concentration were required. Analytical system noise was estimated as the variance of the  $n$  replicate measurements, and LOD was calculated using the equation:

$$LOD = t_{n-1, \alpha/s} S \quad (3)$$

Where  $t_{n-1, \alpha/s}$  is the student  $t$  value for  $n$  replicates at the 95 percent confidence level and  $S$  is an estimate of the standard deviation. For  $n$  values between 5 and 9, the  $t_{n-1, \alpha/s}$  ranged between 2.78 and 2.23. Measurements for LOD calculations were made using the entire ITMS-MIP system in order to determine the expected system performance for in situ applications. The ITMS-MIP system detection limits varied from site to site, but were in the range of 100 to 500  $\mu\text{g/L}$  in groundwater for the 34 VOC analytes listed on the USEPA Target Compound List.

### **Verification sample analytical procedures**

Soil verification samples were analyzed by USEPA Methods 5035 and 8260. All verification samples were analyzed by independent laboratories in accordance with the project Quality Assurance Project Plan (ERDC 1999a,b).

## 5 MIP/DSITMS System Performance Assessment

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This chapter will address the performance-based objectives relative to the data produced and the performance of the ITMS-MIP sensor technology during the demonstrations.

### ITMS-MIP System Data Summary

For this demonstration, ITMS-MIP system data were collected at two geographic locations, Naval Air Station North Island, Coronado, California (July 1999 and April / May 2000) and DOE Savannah River Site, Aiken, South Carolina (September 1999). As discussed earlier, these sites were selected because they were amenable to cone penetrometer investigation and were known to have VOC soil and groundwater contamination. Table 1 contains a summary of the fieldwork conducted at each demonstration site.

<b>Table 1</b> <b>Summary of Field Sampling Conducted at ITMS-MIP Demonstration Sites</b>				
<b>Site (Date)</b>	<b>Number of MIP Penetrations</b>	<b>Number of ITMS-MIP Measurements</b>	<b>Number of Verification Samples</b>	<b>Maximum Depth m (ft)</b>
NAS North Island (July 1999)	40	207	39	23.6 (77)
NAS North Island (April/May 2000)	28	493	19	21.6 (71)
DOE Savannah River Site (September 1999)	5	154	31	34.4 (113)

The April / May 2000 NAS North Island work was performed to gather data and information on the technical capabilities of the ITMS-MIP, but it was also performed as a production job under a dynamic work plan mode of operation. The demonstration served three purposes: (a) it evaluated the technology, (b) it provided NAS North Island with needed site characterization, and (c) it demonstrated the utility of the dynamic work plan approach to site characterization. In addition to placing the technology in the proper context by performing production-mode work, the demonstration provided more realistic data

for cost performance evaluation. Demonstrating the ITMS-MIP during actual production work performed in the dynamic work plan mode better highlighted the technological capabilities while illustrating the significant advantages gained by using onsite decision making with real-time data to reduce the time and cost of site characterization. Figure 8 shows the type of data collected in situ by the soil classification / ITMS-MIP system combination. The analyte is plotted against the soil type with depth. In this example, the soil classification scale ranges from 1 to 12, with clay ranging from 3 to 5, silts ranging from 5 to 8, and sands ranging from 8 to 11.

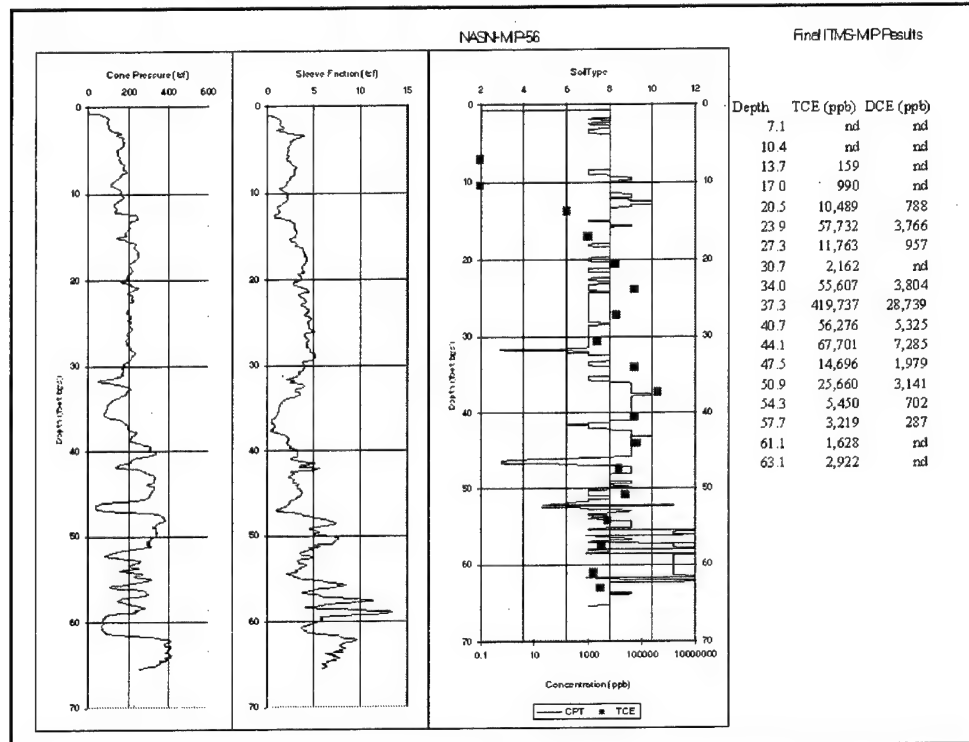


Figure 8. Typical in situ analysis result for an investigation location. VOC results are in µg/l of calibration solution

## ITMS-MIP System Data Assessment

The two 1999 ESTCP demonstration sites produced 73 ITMS-MIP penetrations, over 800 ITMS-MIP analyses, and 89 USEPA Method 8260 validation analyses. Comparisons of the ITMS-MIP results with their corresponding validation analyses are summarized in Appendix B.

Data quality for both the ITMS-MIP and the validation sample analyses were ensured using standard quality assurance procedures including initial system calibration, daily calibration checks, performance evaluation (PE) check standards, blanks, and spike recoveries (for EPA Method 8260 only).

## Comparison Between the ITMS-MIP System and EPA Method 8260

During this demonstration, the MIP/DSITSM was extensively tested with 73 penetrations from 2 geographic locations to depths in excess of 34 m (113 ft) BGS (Table 1). In situ data were collected from soils contaminated with both chlorinated and nonchlorinated analytes with concentrations ranging over four orders of magnitude from single  $\mu\text{g/L}$  to hundreds of  $\text{mg/L}$  (ppb to ppm). Validation of the technique was conducted by sampling soil bores adjacent to the MIP penetration and offsite analysis of the validation samples by EPA Method 8260.

The results of validation sample analysis by EPA Method 8260 for NAS North Island appear to be systematically biased toward the in situ ITMS-MIP results. Figures 9 and 10 show that the ITMS-MIP results were greater than validation sample results for all soil types with a combined  $R^2$  of 0.48 and a slope of 0.78. However, actual correlation bias cannot be determined when comparisons are based on different concentration units. Since the ITMS-MIP results are expressed in  $\text{mg/L}$  of calibration solution, which is an apparent concentration term, relative mass of contaminants between CPT pushes is measured and not the true soil concentrations as measured by conventional laboratory analysis.

Figure 9 presents data collected by two different operators from successive years. It is believed that some bias may be related to the process of collecting soil samples from the NAS North Island site. This belief is supported by the results obtained from collecting water samples from short screen length 0.6-m (2-ft) micro-wells as presented in Table 2. While there may not be exact agreement between the water sample results and the in situ ITMS-MIP results from the saturated zone, they compare more favorably with an  $R^2$  of 0.95 compared to samples from the vadose zone with an  $R^2$  of 0.60 (Figure 10). The ITMS-MIP system correctly indicated the presence of contamination without false negative results. However, one false positive ITMS-MIP measurement was recorded at MIP41-70 (Table 2). It should be noted that sand matrix materials provided better correlation regarding the ITMS-MIP data reliability than other soil matrix materials.

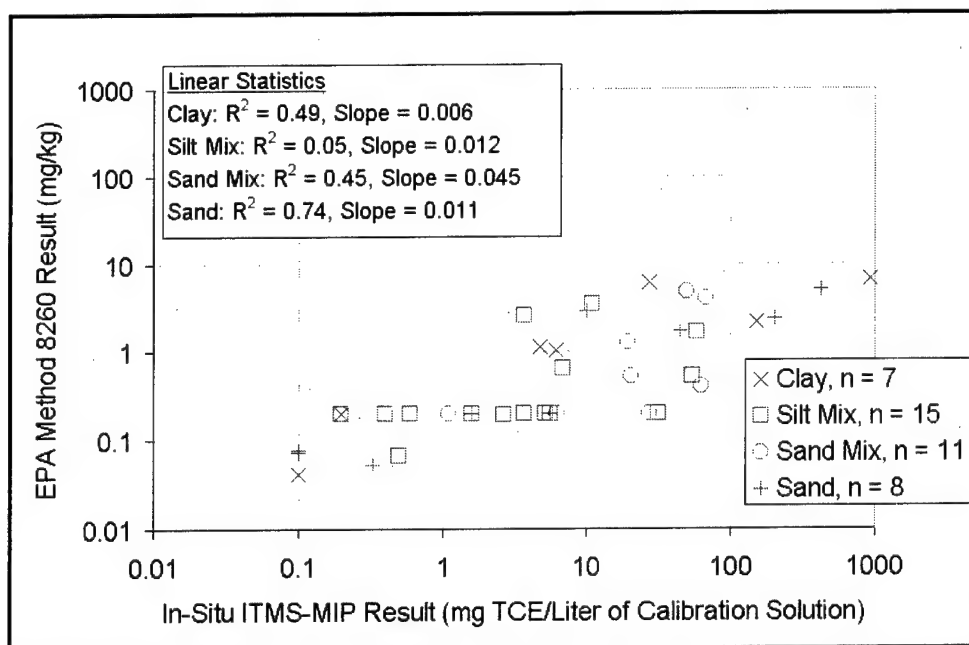


Figure 9. NAS North Island validation results by soil type for TCE

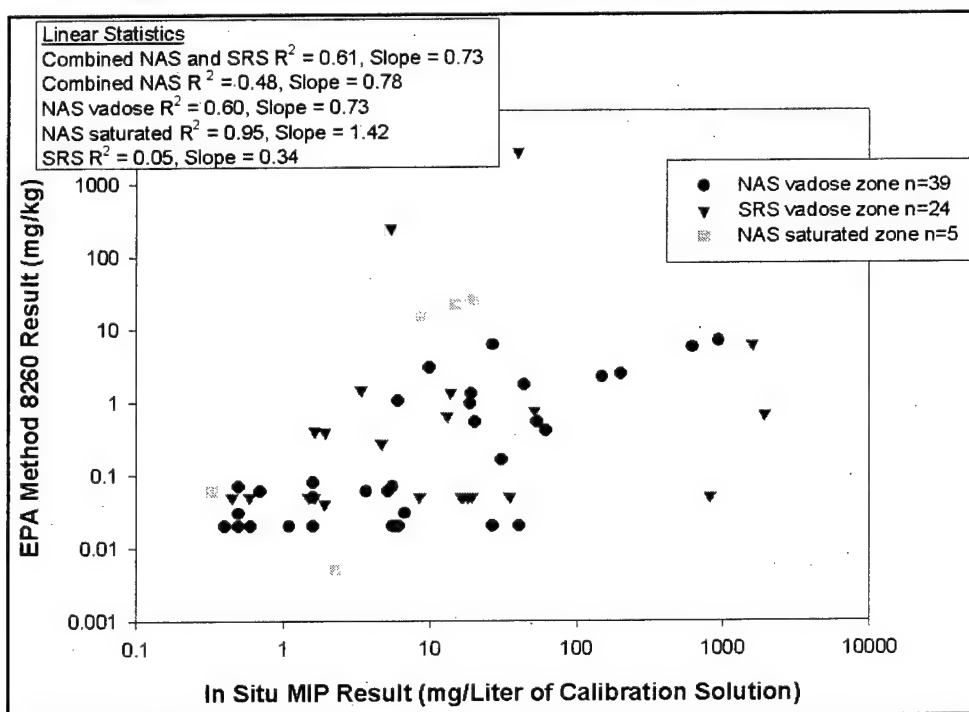


Figure 10. NAS North Island and DOE SRS combined validation results

**Table 2**  
**TCE Saturated Zone Water Sample Comparison NAS North Island,**  
**May 2000**

Sample ID	MIP Sample Depth ft BGS	ITMS-MIP ug/L	Screen Length ft BGS	EPA Method 5035/8260 ug/L
MIP41-43	40.6	331	40-43	60
MIP41-70	71.1	2294 <sup>1</sup>	68-70	<5
MIP46-54	54.2	8785	54-56	15200
MIP55-30	30.5	19923	30-32	25400
MIP55-45	44.1	72688	45-47	22100
MIP55	47.4	14839		

<sup>1</sup>Soil sample collected from MIP41-70 had low moisture content; false positive.

The results of validation sample analysis by USEPA Method 8260 for SRS do not correlate with in situ ITMS-MIP results. Figure 11 shows that the ITMS-MIP results were greater than validation sample analysis results from all soil types except clay. The ITMS-MIP results tended to underestimate the validation sample analysis results for clay type soils. The results from SRS demonstrate that the current ITMS-MIP calibration method that uses saturated sand is inappropriate for vadose zone soils with low moisture content.

The purpose of the ITMS-MIP is to rapidly screen subsurface soil and water for VOC contamination. As a qualitative screening tool, the ITMS-MIP system was successful. Only one false positive ITMS-MIP measurement was produced from a low moisture soil at NAS North Island.

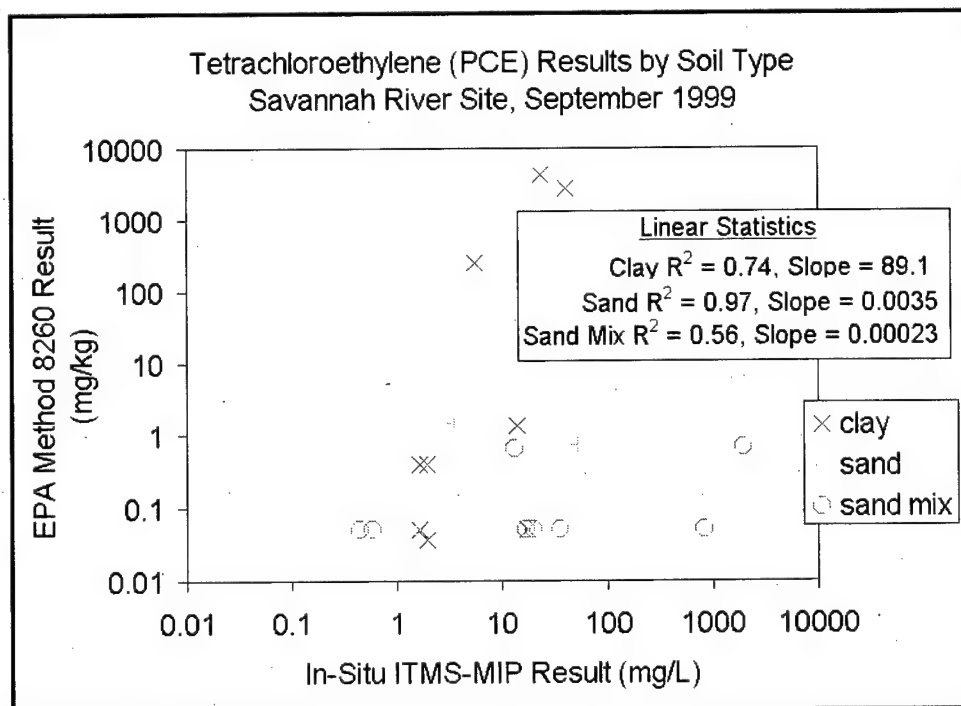


Figure 11. SRS validation results by soil type for PCE



## Sample Matrix Effects on ITMS-MIP System

The sample matrix investigated using the ITMS-MIP system was soil and soil gas in the vadose zone and soil and water in the saturated zone. The ITMS-MIP system response in saturated and vadose zone soils was different when compared with validation sample results. There were no observable matrix effects in saturated soils (Figure 10) where the saturated zone  $R^2$  was 0.95 and the slope was 1.42. However, vadose zone soil types were observed to effect ITMS-MIP with less than acceptable quantitative results at the NAS North Island and at the DOE SRS (vadose zone  $R^2 = 0.60$  for NAS and  $R^2 = 0.05$  for SRS). The ITMS-MIP overestimated contaminant concentrations for most vadose zone soils at the SRS when compared with the validation results but underestimated contaminant concentrations for clay type vadose zone soils at both sites (Figures 9 and 11).

Field demonstrations at five locations were conducted to determine if variations in soil matrix affected the functionality of the ITMS-MIP system. Soil stratigraphy data verified that the sites exhibited different soils types and were heterogeneous in subsurface soil composition. The combined validation data presented in Figure 12 show that soil matrix effects were much larger in unsaturated subsurface media than in saturated media. Linear statistics for the combined five sites show an  $R^2$  of 0.34 and a slope of 0.14. The utility of the ITMS-MIP system for qualitative screening of sites for VOC contamination was demonstrated.

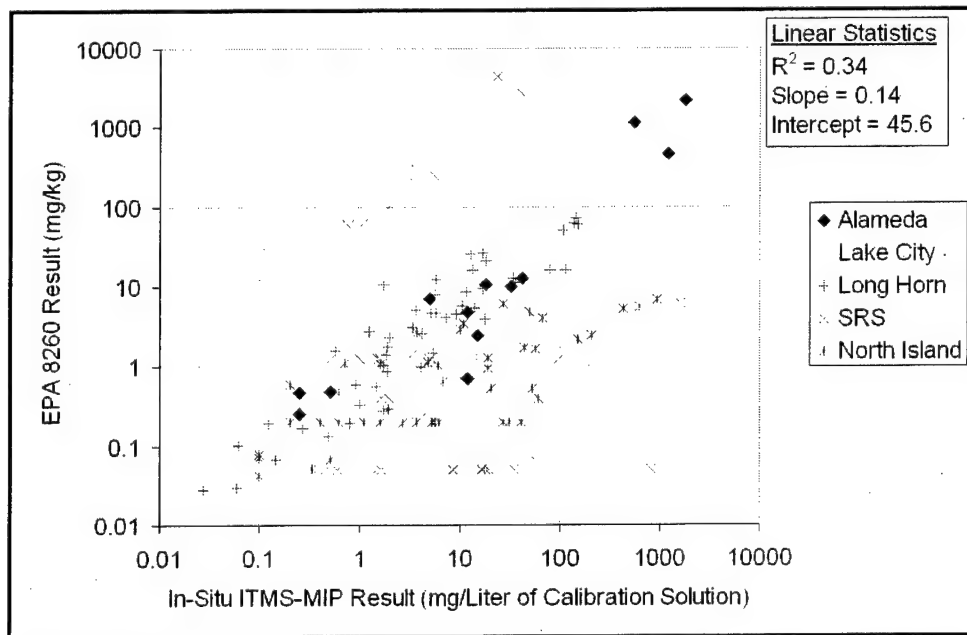


Figure 12. Comparison of co-located samples from five ITMS-MIP sites

## 6 Cost Assessment

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### ITMS-MIP System Cost Performance

The costs associated with ITMS-MIP operation include equipment cost for the SCAPS truck, expendable supplies, crew travel expenses, and labor. While these costs vary from site to site, the average cost of operating a SCAPS truck and four-person crew in the field during production work, regardless of sensor type, is \$4,500 per day.

The cost per ITMS-MIP system data point (unit cost) depends on the number of sensor penetrations (unit operations) completed per day. The number of penetrations per day achievable at a particular site depends on site mobility, subsurface geology, and depth of penetration. As previously discussed, the DSITMS analysis is very fast (less than 5 min per measurement). The majority of the time associated with a unit operation of the ITMS-MIP system is the time associated with pushing to depth. The deeper the average penetration depth pushed at a particular site, the lower the unit production rate and the higher the unit cost. However, it should be noted that the same unit production/unit cost relationship exists for conventional monitoring well installation and groundwater sampling or placement and sampling of bore holes.

### Cost Comparison of the ITMS-MIP to Conventional Technologies

Table 3 shows cost comparisons between the ITMS-MIP technology and conventional drilling/soil sampling. Cost savings are realized from SCAPS direct push methods due to a number of factors: (a) the speed with which direct push techniques access depth compared with drilling, (b) the low amount of investigation-derived waste produced by the direct push methods, and (c) the rapid availability of near real-time information can be utilized to make additional sample placement decisions. As can be seen from Table 3, the MIP provides significant cost savings compared to conventional drilling/soil sampling with offsite analysis.

**Table 3**  
**Comparison of Unit Costs for the ITMS-MIP System and**  
**Conventional Technologies**

SCAPS ITMS-MIP In Situ Measurement		Conventional Drilling (hollow stem auger, split spoon, and offsite analysis)		Direct Push and Offsite Analysis	
10 pushes to 30 ft, MIP VOC analysis every 3 ft	Cost	10 borings to 30 ft (100 soil samples for VOC analysis)	Cost	10 borings to 30 ft (100 soil samples for VOC analysis)	Cost
2 field days @ \$4500/day	\$9,000	Drilling for 300 ft @ \$30/ft	\$9,000	Drilling for 300 ft @ \$10/ft	\$3,000
Analysis for 100 samples	Included in cost	VOC analysis for 100 samples @ \$200/sample	\$20,000	VOC analysis for 100 samples @ \$200/sample	\$20,000
Geotechnical data: CPT continuous data for 300 ft	Included in cost	Geotechnical analysis for 10 samples @ \$100/sample	\$1,000	Geotechnical analysis for 10 samples @ \$100/sample	\$1,000
1 waste drum @ \$40/drum	\$40	28 waste drums @ \$40/drum	\$1,120	1 waste drum @ \$40/drum	\$40
Decon water testing	\$1,000	Decon water testing	\$1,000	Decon water testing	\$1,000
Waste soil testing	\$0	Waste soil testing	\$3,000	Waste soil testing	\$0
Waste soil disposal	\$0 (none produced)	Waste soil disposal for 20 drums @ \$100/drum	\$2,000	Waste soil disposal	\$0 (none produced)
Decon water disposal for 1 drum @ \$100/drum	\$100	Decon water disposal for 8 drums @ \$100/drum	\$800	Decon water disposal for 1 drum @ \$100/drum	\$100
4-man crew	Included in cost	Geologist for 40 hr @ \$60/hr	\$2,400	Geologist for 24 hr @ \$60/hr	\$1,440
		Technician for 40 hr @ \$40/hr	\$1,600		
<b>TOTAL</b>	<b>\$10,140</b>	<b>TOTAL</b>	<b>\$41,920</b>	<b>TOTAL</b>	<b>\$26,580</b>
Unit cost per sample	\$101	Unit cost per sample	\$419	Unit cost per sample	\$266
Note: To obtain meters, multiply feet by 0.3048.					

## 7 Regulatory Issues

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The MIP module was developed, manufactured, and patented by Geoprobe Systems, Inc., of Salina, KS. Geoprobe Systems is not currently seeking regulatory acceptance of the MIP. The objective of this ESTCP-sponsored demonstration was to gather high-quality data that could be used to demonstrate the utility of the ITMS-MIP before transition to the USACE Districts. The DSITMS, the final detector for the MIP, has undergone extensive review and certification by regulatory agencies such as the USEPA OSHW, the California EPA, and the Interstate Technology Regulatory Cooperation Workgroup.

## 8 Technology Implementation

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### DoD Requirements for VOC Site Characterization

A large number of sites at DoD installations are known to be contaminated VOCs including chlorinated solvents and BTEX. The USEPA surveyed site remediation needs within Federal and state agencies and has published the results of this survey (Happel, Bechanbach, and Halden 1997). This survey reported 8,300 DoD sites that require remediation at 2,000 installations. Of the reported sites, 65 percent contained VOCs.

The vadose zone is a particularly difficult region to characterize because VOC contaminants can exist in either vapor or liquid phase depending on the makeup of the soil strata. In the past, traditional methods of site characterization (collecting a soil sample and sending it to an offsite laboratory for analysis) have underestimated the magnitude of the problem. Past protocols recommended by USEPA SW-846 Method 5030 (USEPA 1995) often resulted in a 90 to 99 percent loss of VOCs from soil samples prior to laboratory analysis (Hewitt and Lukash 1997). While Method 5030 has been replaced with alternative methods for in-vial sample collection and analysis, such as USEPA SW-846 Methods 5035 and 5021 (USEPA 1995), much of the site characterization data available were based on the older, less reliable method. Hence, the extent of vadose zone VOC contamination may be much greater than currently believed.

Under the right scenario, the ITMS-MIP technology could also prove to be a useful tool for monitored natural attenuation (MNA) remediation. Remediation of chlorinated solvents and fuel spills consists of removal of the source of contamination as much as is practical and containment, treatment, or removal of the dissolved or sorbed contamination from the groundwater or soil. Under the proper conditions at some sites, MNA can contribute significantly to remediation of VOC contamination, and it may accomplish site remediation goals at a lower cost than conventional remediation technologies within similar time frames (USEPA 1999a,b). As of 1995, MNA was the second most popular remediation option for soil sites. It is being used at roughly 29,000 sites (USEPA 1998). The MIP/ITMS technology's ability to precisely locate and sample critical geologic strata makes it an ideal tool to monitor natural attenuation VOC remediation.

## **ITMS-MIP System Transition**

The MIP technology, using nonselective detectors, is becoming widely used in the commercial sector. Interfaced with the DSITMS, the ITMS-MIP sensor technology has been transitioned as a screening tool to the USACE Kansas City, Savannah, and Tulsa Districts SCAPS programs and to the Navy Public Works Center San Diego SCAPS program.

## 9 Conclusions

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The ITMS-MIP system is a rapid in situ qualitative analytical tool for gathering large amounts of data in a short period of time. This type of data can be synthesized onsite for immediate use in the decision making process for site characterization. During the April / May NAS North Island investigation, the SCAPS ITMS-MIP crew analyzed 493 individual MIP samples in situ from 28 sites in 15 days. Using the Bioventing Cost Estimator, it was estimated that the placing of 28 monitoring wells to evaluate the same 28 locations would take a drill crew 2 months to accomplish. The large difference in the number of samples made available by the ITMS-MIP system provides the basis of a broader profile of the contaminant plume than does sampling by conventional methods.

The ITMS-MIP system has been used in a variety of soil and soil moisture conditions. The sample matrix investigated was soil and soil gas in the vadose zone and water in the saturated zone. The ITMS-MIP system response in saturated and vadose zone soils was different when compared with validation sample results. The system appears to provide the most quantitative results in the saturated zone ( $R^2 = 0.95$ ). The vadose zone soil types were observed to affect the ITMS-MIP with less than acceptable quantitative results at the NAS North Island and at the DOE SRS (vadose zone  $R^2 = 0.60$  for NAS North Island and  $R^2 = 0.010$  for SRS). The ITMS-MIP overpredicted contaminant concentration for most vadose zone soils at the SRS when compared with the validation results but underpredicted contaminant concentrations for clay type vadose zone soils at both sites. This may be because of the method of calibrating the MIP using saturated sand. Combined data for the five ITMS-MIP sites show an  $R^2$  of 0.34 and a slope of 0.14.

The ITMS-MIP can be operated in any environment and soil type that are amenable to conventional drilling or direct push technologies. Problems with downtime due to rupture of the MIP polymer membrane have been resolved with the development of the field replaceable membrane port.

# 10 Recommendations

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Site Quality Assurance Project Plans should include adequate validation samples since the ITMS-MIP system is a qualitative analytical tool. Standard quality assurance procedures prescribe 10 percent verification. This frequency can be increased when sampling in the vadose zone or when sampling near site action levels. The ITMS-MIP calibration method should be reexamined to improve the correlation of ITMS-MIP data to that of USEPA methods for vadose zone soils. Further evaluation of the amount of in situ soil actually sampled by the MIP could also result in improved data correlation in both the vadose and saturated zones.



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# Appendix A

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# **Appendix B**

## **ITMS-MIP Site Data Summary Tables**

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This appendix presents the following ITMS-MIP site data summary tables:

- a.* Table B1 – TCE Soil Sample Comparison Data for Naval Air Station North Island
- b.* Table B2 – TCE Water Sample Comparison Data for Naval Air Station North Island
- c.* Table B3 – PCE Soil Comparison Data for Department of Energy Savannah River Site

**Table B1**  
**TCE Soil Sample Comparison Data for Naval Air Station, North Island**

Sample ID	Depth ft BGS	Raw ITMS Counts	Calibration Factor mg/L of TCE per count	Background Count	MIP/DSITMS mg/L	EPA 5035/8260 mg/kg
MIP11	35	723	0.0002011	1407	<0.5	<0.02
MIP11	45	134564	0.0002011	1407	27.00	6.10
MIP11	50	750593	0.0002011	1407	150.00	2.20
MIP11	53	4641479	0.0002011	1407	933.00	6.80
MIP16	25	5571	0.0003759	1415	1.60	0.08
MIP16	35	52376	0.0003759	1415	19.20	1.28
MIP16	45	34439	0.0003759	16385	6.80	0.03
MIP35	25	1561	0.0005865	1359	<0.5	<0.02
MIP35	35	2775	0.0005865	1828	0.60	0.02
MIP35	43.7	2648	0.0005865	1972	0.40	0.02
MIP35	50	4148	0.0005865	3132	0.60	0.02
MIP30	25	3165	0.0003759	2616	<0.5	<0.02
MIP30	40.7	3133	0.0003759	1880	0.50	0.07
MIP30	45	7070	0.0003759	2788	1.60	0.05
MIP30	50	4741	0.0003759	2882	0.70	0.06
MIP04	25	3202	0.0004063	1529	<0.5	<0.02
MIP04	30	5478	0.0004063	1529	1.60	<0.02
MIP04	35	10590	0.0004063	1529	3.70	0.06
MIP04	38.5	15376	0.0004063	1529	5.60	0.07
MIP04	43.5	14355	0.0004063	1529	5.20	0.06
MIP04	50	5198	0.0003759	2818	<0.5	<0.02
MIP19	25	1563	0.0003759	480	0.40	<0.02
MIP19	35	1569	0.0003759	480	0.40	<0.02
MIP19	45	3416	0.0003759	480	1.10	<0.02
MIP19	50	16647	0.0003759	500	6.10	1.05
MIP19	54	29287	0.0003759	2628	10.00	2.94
MIP33	25	6203	0.001230	6708	<0.5	0.03
MIP33	35	13078	0.001230	8028	6.20	<0.02
MIP33	45	58961	0.001230	8528	62.00	0.40
MIP33	50	59429	0.001230	15480	54.00	0.53
MIP33	55	13837	0.001230	9318	5.60	<0.02
MIP39	7	168562	0.0003759	58618	41.00	<0.02
MIP39	12	83163	0.0003759	7030	31.00	0.16
MIP39	17	71156	0.0003759	664	27.00	<0.02
MIP39	35	541184	0.0003759	1204	203.00	2.42
MIP39	37	117818	0.0003759	778	44.00	1.71
MIP39	42	54497	0.0003759	33	20.50	0.53
MIP06	25	48540	0.0004063	1013	19.00	0.95
MIP06	35	1551342	0.0004063	27053	619.00	5.56

Note: Calibration factor is determined each day using the calibration procedure as detailed in Chapter 4. Background count is determined during the calibration procedure (ITMS response to soil water matrix). In some instances the background concentration is increased if operator suspects that carry-over contamination is present (for example, MIP16 at 45 ft BGS). The concentration of TCE is determined by subtracting background counts from the raw ITMS counts and multiplying by the calibration factor.



**Table B2**  
**TCE Water Sample Comparison Data for Naval Air Station, North Island**

Sample ID	MIP Sample Depth ft BGS	Raw ITMS Counts	Calibration Factor ug/L of TCE per count	Background Count	MIP/DSITMS ug/L	Screen Length ft BGS	EPA 5035/8260 ug/L
MIP41-43	40.6	1337	0.283388	168.5705	331	40-43	60
MIP41-70	71.1	5935	0.391831	80.16795	2,294*	68-70	<5
MIP46-54	54.2	31170	0.283388	168.5705	8,785	54-56	15200
MIP55-30	30.5	43694	0.456798	80.16795	19,923	30-32	25400
MIP55-45	44.1	159206	0.456798	80.16795	72,688	45-47	22100
MIP55	47.4	32565	0.456798	80.16795	14,839		

\* Soil sample collected from MIP41-70 had low moisture content; false positive.

**Note: Reason for Different Calibration Factor and Background Count**

Sample ID	Date Completed	
MIP41-43	4/18/00	Initial calibration on 4/18/00
MIP41-70	4/30/00	New MIP, calibration on 4/29/00
MIP46	4/19/00	Initial calibration on 4/18/00
MIP55	4/25/00	The result of the post MIP-48 QA check was two standard deviations off the 4/18/00 calibration curve. An abbreviated calibration event was performed on 4/20/00.

**Table B3**  
**PCE Soil Comparison Data for DOE Savannah River Site**

Sample ID	Depth ft BGS	Raw ITMS Counts	Calibration Factor mg/L of PCE per count	Background Count	MIP/DSITMS mg/L	EPA 5035/8265 Onsite ITMS Results mg/kg
SRS02	10.9	4718	0.000425838	218	1.92	0.04
SRS05	14.1	4786	0.000425838	218	1.94	0.39
SRS06	17.4	94245	0.000425838	218	40.04	2727.6
SRS07	19.8	55379	0.000425838	218	23.49	4350.4
SRS08	23.9	12999	0.000425838	218	5.44	248.1
SRS09	27.2	3734363	0.000425838	218	1590.14	5.98
SRS10	33.6	4537882	0.000425838	218	1932.31	0.66
SRS13	37.0	1918085	0.000425838	218	816.70	< 0.05
SRS14	56.7	40289	0.000425838	218	17.06	< 0.05
SRS15	63.0	39046	0.000425838	218	16.53	< 0.05
SRS16	40.3	13414	0.000128550	650	1.64	0.4
SRS18	47.2	405273	0.000128550	650	52.01	0.74
SRS19	53.4	275753	0.000128550	650	35.36	< 0.05
SRS20	53.7	102997	0.000128550	650	13.16	0.64
SRS21	57.0	152424	0.000128550	650	19.51	< 0.05
SRS22	57.7	37180	0.000128550	650	4.70	0.27
SRS23	63.6	66744	0.000128550	650	8.50	< 0.05
SRS24	95.3	13326	0.000128550	650	1.63	< 0.05
SRS26	96.5	27205	0.000128550	650	3.41	1.47
SRS27	101.0	109023	0.000128550	650	13.93	1.33
SRS28	101.6	143249	0.000128550	650	18.33	< 0.05
SRS29	108.3	12214	0.000128550	650	1.49	< 0.05
SRS30	108.9	5245	0.000128550	650	0.59	< 0.05
SRS31	109.5	4125	0.000128550	650	0.45	< 0.05

**Note: Reason for Different Calibration Factor and Background Count**

Sample ID	Date Completed	
SRS02 - SRS15	8/30/99	Initial calibration on 8/27/99
SRS16 - SRS31	9/03/99	New MIP, calibration on 9/02/99

# Appendix C

## Notation

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AEC	U.S. Army Environmental Center
ASTM	American Society for Testing and Materials
BETX	Benzene, ethyl benzene, toluene, xylene
BGS	Below ground surface
CI	Chemical Impact Ionization
CPT	Cone Penetrometer Test
DCE	Dichloroethene
DNAPL	Dense non-aqueous phase liquid
DoD	Department of Defense
DOE	Department of Energy
DSITMS	Direct Sampling Ion Trap Mass Spectrometer
EI	Electron Impact Ionization
ERDC	U.S. Army Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
ID	Inner diameter
IDW	Investigation derived waste
ITMS	Ion Trap Mass Spectrometer
ITRC	Interstate Technology Regulatory Cooperation
LIF	Laser induced fluorescence

LNAPL	Light non-aqueous phase liquid
LOD	Limit of detection
MIP	Membrane Interface Probe
MNA	Monitored natural attenuation
$m/z$	Mass to charge ratio of an ion
$n$	Number of replicate analyses
NAS	Naval Air Station
OD	Outer diameter
ORNL	Oak Ridge National Laboratories
OSHW	USEPA Office of Solid and Hazardous Waste
PCE	Tetrachloroethene
PE	Performance evaluation
PEEK	Polyether ether ketone
POL	Petroleum, oil, and lubricant
ppb	Parts per billion; equivalent to ng/g and $\mu\text{g/L}$
ppm	Parts per million; equivalent to $\mu\text{g/g}$ and mg/L
$R^2$	Correlation coefficient
S	Estimate of standard deviation
SRS	Savannah River Site
SCAPS	Site Characterization and Analysis Penetrometer System
SCN	Soil class number
$t$	Student $t$ value
TCE	Trichloroethene
TFE	Tetrafluoro ethylene or Du Pont's Teflon
TPH	Total petroleum hydrocarbons
USACE	U.S. Army Corps of Engineers

USEPA	U.S. Environmental Protection Agency
UST	Underground storage tanks
VOC	Volatile organic compound

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<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b>  Site characterization for subsurface contaminants is time consuming and costly. The Site Characterization and Analysis Penetrometer System (SCAPS) Ion Trap Mass Spectrometer - Membrane Interface Probe (ITMS-MIP) system was developed to respond to the need for real-time, in situ measurements of subsurface volatile organic compound (VOC) contamination at hazardous waste sites. The ITMS-MIP system performs rapid field screening to determine the presence or absence of subsurface volatile organic contaminants. The Membrane Interface Probe developed by Geoprobe Systems, Inc., was coupled with the direct sampling ITMS to provide in situ measurement of VOCs in the subsurface. The ITMS-MIP system was demonstrated at five geographically different hazardous waste sites. The ITMS-MIP was found to perform best in saturated soils. Results from the saturated zone show a good correlation with U.S. Environmental Protection Agency validation methods for co-located samples with a linear regression coefficient of 0.95 and a slope of 1.42 for trichloroethene. Correlations for vadose zone samples showed differences in soil types and moisture content. The ITMS-MIP was successfully demonstrated as a qualitative screening tool at these sites. The SCAPS ITMS-MIP system was demonstrated to reduce the time and cost required to characterize sites by directing the placement of a reduced number of conventional soil bores and monitoring wells.					
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